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ORIGINAL PAPER

Review on Catalytic Cleavage of C–C Inter-unit Linkages in Lignin Model Compounds: Towards Lignin Depolymerisation

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Abstract
Lignin depolymerisation has received considerable attention recently due to the pressing need to find sustainable alternatives to fossil fuel feedstock to produce chemicals and fuels. Two types of interunit linkages (C–C and C–O linkages) link several aromatic units in the structure of lignin. Between these two inter-unit linkages, the bond energies of C–C linkages are higher than that of C–O linkages, making them harder to break. However, for an efficient lignin depolymerisation, both types of inter-unit linkages have to be broken. This is more relevant because of the fact that many delignification processes tend to result in the formation of additional C–C inter-unit bonds. Here we review the strategies reported for the cleavage of C–C inter-unit linkages in lignin model compounds and lignin. Although a number of articles are available on the cleavage of C–O inter-unit linkages, reports on the selective cleavage of C–C inter-unit linkages are relatively less. Oxidative cleavage, hydrogenolysis, two-step redox-neutral process, microwave assisted cleavage, biocatalytic and photocatalytic methods have been reported for the breaking of C–C inter-unit linkages in lignin. Here we review all these methods in detail, focused only on the breaking of C–C linkages. The objective of this review is to motivate researchers to design new strategies to break this strong C–C inter-unit bonds to valorise lignins, technical lignins in particular.

Keywords C–C bond cleavage · Lignin valorisation · Catalytic depolymerisation · Lignin model compounds · Technical lignins

1 Introduction

1.1 Biorefineries and Lignin Valorisation

The greatest challenge our society faces is the increased demand for energy and commodity chemicals because of population growth along with the increasing demand from emerging large economies [1]. This scenario is further complicated by the depletion of conventional fossil fuel based feedstock to produce them, the greenhouse effect and consequent climate changes [2]. There is a pressing demand to address the chemical and energy security issues without compromising the environment. One of the proposed alternatives for achieving this is to use green and sustainable alternatives to the conventional feedstock for producing commodity chemicals and fuels. The fuel versus food debate for the 1st generation biofuels led to the development of 2nd generation biofuels where, lignocellulosic biomass (or waste biomass) that does not compete with food crops, is used as the feedstock to produce chemicals and fuels [3–5].

Integrated conversion of all the components of lignocellulosic biomass (cellulose, hemicellulose and lignin) in a biorefinery, analogous to a petroleum refinery, to value-added products has been proposed by the International Energy Agency (IEA) to make them economically viable and sustainable [6]. Cellulose is a semi-crystalline homopolysaccharide comprised of unbranched D-glucose (anhydroglucose) units linked at the first and fourth carbon atoms through β-glycosidic bonds (β–1,4 glycosidic bonds) whereas hemicellulose is an amorphous polysaccharide branched with short lateral chains consisting of various different sugars [7]. Lignin, the third component of lignocellulosic biomass, is found in all vascular plants, and is, after cellulose, the most abundant carbon source on earth [8]. It is a naturally amorphous polymer that gives plants their structural strength and shape. Lignin contains highly functionalised aromatic units that makes them a potential sustainable

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feedstock to produce aromatics. It fills the space between the hemicellulose and cellulose, making up the final lignocellulose structure, offering strength through cross-linkages with the carbohydrate polymers (Fig. 1) [7]. Until now, valorisation of both polysaccharides cellulose and hemicellulose have been extensively studied and successfully practised in the industrial production of biofuel (bioethanol, biohydrogen and biogas) [9] and bio-based chemicals and material (such as biopolymers) [10–13].

However, in most of these processes the residual lignin is often burnt as a low grade fuel for power generation or steam production or used as low value products such as dispersing, binding or emulsifying agents, phenolic resins, carbon fibres, wood panel products, automotive brakes and epoxy resins [7, 14]. Lignin is of particular interest because it contains several highly functionalised aromatic moieties. It is the only large volume renewable source of aromatics or platform chemicals [BTX (benzene, toluene and xylene), phenols, and aliphatic fractions (C1-3)]. Bulk chemicals can be produced from these sustainably produced BTX without changing the current processes and technologies [7, 13, 15]. Economically, converting lignin into fully deoxygenated BTX may not be highly desirable because in certain processes BTX are again oxidised. Hence strategies to valorise lignin, that can preserve the aromatic rings and functionalities present have to be developed. The resultant small aromatic molecules can be used in existing or new routes to produce base chemicals [16].

Lignin consists of several aromatic sub-units: p-hydroxyphenyl type (H), guaiacyl type (G) and syringyl type (S) and they are the result of the polymerization of three types of phenylpropane units that are considered to be the primary building blocks of lignin and are called as monolignols [17]. The monolignols differs from each other in the number of methoxy groups attached to the aromatic ring (none, one or two methoxy groups in the p-coumaryl, coniferyl and synapyl alcohol respectively) (Fig. 2) [18, 19]. The monolignol ratios depend on the type of biomass [18]. In general, hardwood lignin contains mainly G and S units and traces of H units, whereas softwood lignin contains G units predominantly with very low H units, and in the case of grass based lignin nearly equal amounts of G and S units are found with very less H units. Compared to hardwood and softwood lignins, grass lignins contain more H units [7, 17, 20]. For any given lignin sample, the H:G:S ratio can be calculated using wet chemical methods such as acidolysis, nitrobenzene oxidation (NBO), permanganate oxidation, cupric oxide and thioacidolysis [21–23] or spectroscopic techniques such as FT-IR [24] or 2D-NMR [25, 26]. For example, a method for the quantitative analyses of lignin samples was reported by Kline et al. using their normalized Fourier Transform Infra-Red (FTIR) spectra [24]. They assigned the peaks at 1327 and 1267 cm^{-1} to G units, the peaks at 1223 and 1123 cm^{-1} to S units and the

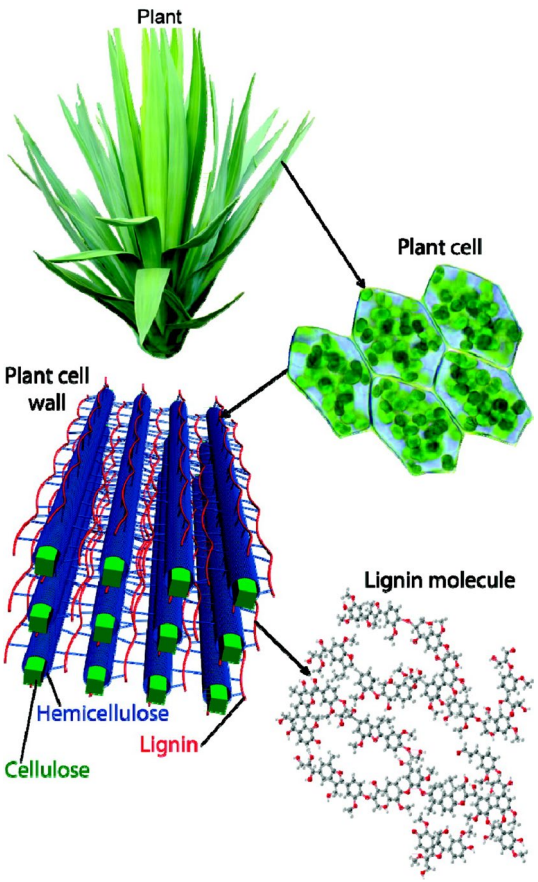


Fig. 1 Representation of the location of lignin in a plant. (Reproduced with permission from reference [7]. Copyright 2010, American Chemical Society)

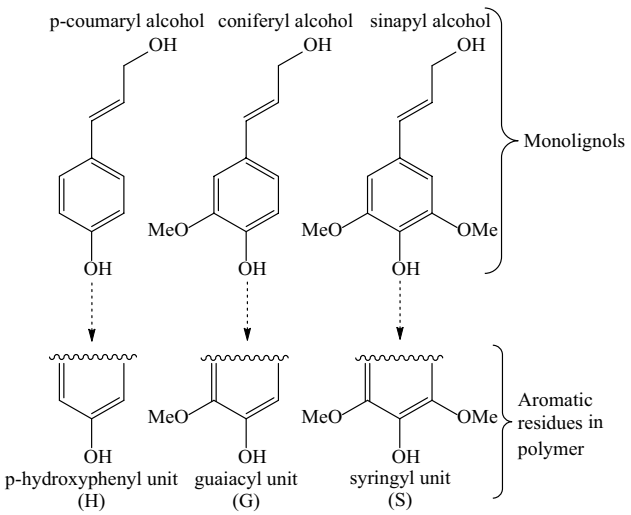


Fig. 2 Monolignol structures and their corresponding residues in lignin polymers. (Adapted from reference [17])

1167 cm^{-1} peak to H units [24]. S/G molar ratios can also be semi-quantitatively estimated by Heteronuclear Single Quantum Coherence (HSQC) 2D-NMR spectroscopy [25, 26].

The diversity in lignin structures is not only because of the difference in the ratio of monolignols, but also because of the way in which these monolignols are covalently linked with each other, called inter-unit linkages. These inter-unit linkages are a combination of C–O and C–C inter-unit linkages [7, 17, 27]. Typical C–O and C–C inter-unit linkages, present in softwood lignin, are highlighted in Fig. 3. It is crucial to have a fairly good understanding on the relative strengths of these inter-unit linkages in order to design methodologies to break them.

Huang et al. used density functional theory (DFT) calculations on 63 representative lignin model compounds to predict the bond dissociation energies (BDE) of different types of inter-unit linkages present in lignin [29]. Table 1 contains the BDE data along with the common names and structures of different lignin model compounds having different inter-unit linkages. This table further contains the abundance of each linkage for different lignocellulosic biomass (softwood, hardwood and grass). C_5–$C_{5'}$ having a BDE around 115–118 kcal/mol, is the strongest of all inter-unit linkages. All C–C inter-unit linkages are stronger than C–O linkages making them more challenging to break [18].

1.2 Native Lignins

In natural or native lignins, as it is present in the raw plant biomass, two-thirds or more of the total inter-unit linkages are C–O linkages, especially (β–O–4) ether bonds, while the rest are C–C inter-unit linages [20]. As mentioned previously, the native structure of lignin varies from plant to plant and in some cases within the same plant, it differs from one part of the plant to the other. It is important to highlight that it has not yet been possible to isolate the real native lignin from plant tissues since the structure always modifies during the lignin isolation process [30]. Using advanced NMR techniques the structures of complex native lignins, in whole cell wall, have been studied in great detail [31]. Another way to study the structure of native lignins is by careful chemical degradation techniques such as thioacidolysis or from milled wood lignin (MWL), which is usually considered to be more or less representative of native lignin [32, 33]. Efforts are currently being made to separate native lignins from biomass with minimal structural changes [18, 34]. It has also been

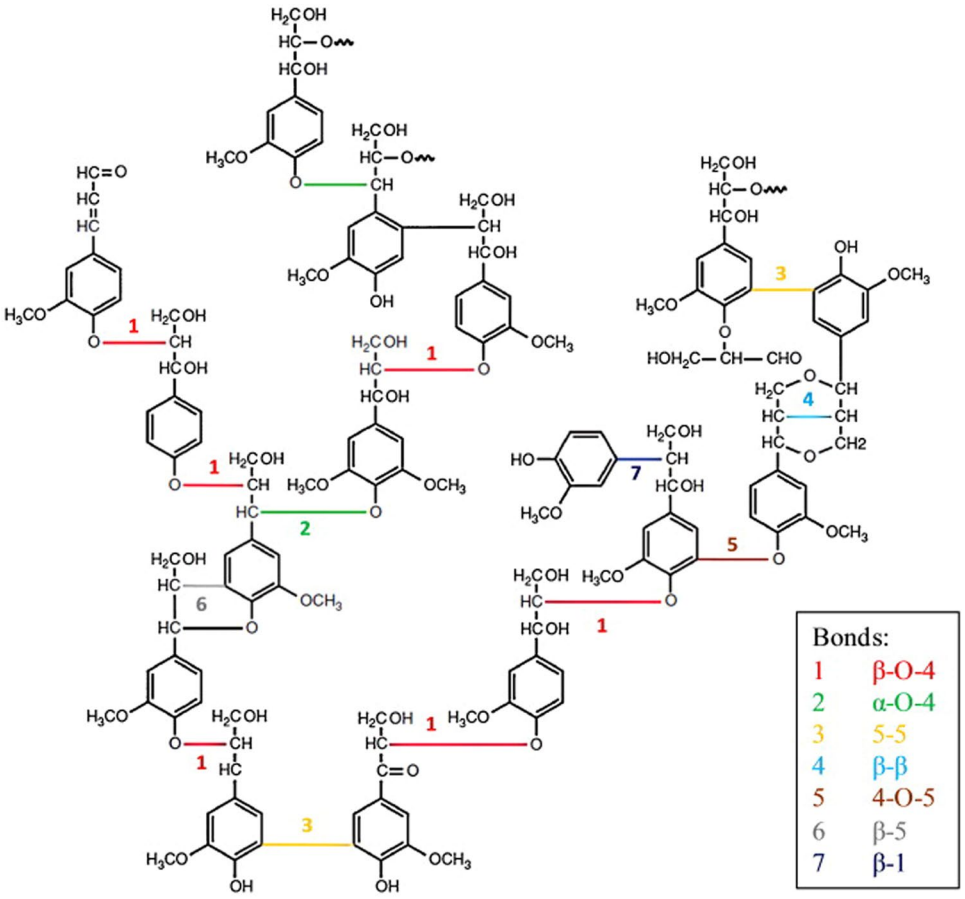
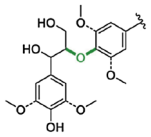
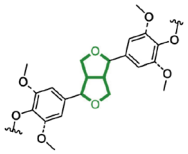
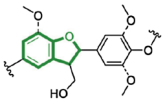
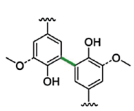
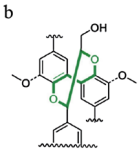
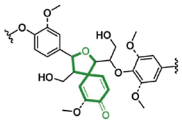
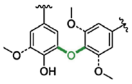


Fig. 3 Typical inter-unit linkages present in softwood lignin. (Reproduced with permission from reference [28]. Copyright 2012, Elsevier)

Table 1 List of lignin model compounds representing various inter-unit linkages, their structure, abundance and bond dissociation energies (Adapted from reference [18])

Name	β-aryl ether	Resinol	Phenylcoumaran	Biphenyl + Dibenzodioxocin	Spirodienone	Diaryl ether
Structure				a  b 		
Inter-unit linkage	β–O–4	(β–β) + (γ–O–α)	(β–5) + (α–O–4)	5–5[a] (5–5) + (α–O–4) + (β–O–4)[b]	β–1 + (α–O–α)	4–O–5
Softwood (%)	45–50	2–6	9–12	5–7[b]	1–9	2
Hardwood (%)	60–62	3–16	3–11	< 1[b]	1–7	2
Grasses (%)	74–84	1–7	5–11	n.d	n.d	n.d
BDE (kcal/mol)	C_β–O–$C_{4'}$ 54–72 C_α–C_β 75–80	C_α–O 68 C_α–C_β 67 C_γ–O 79 C_β–C_β 81	C_α–O–$C_{4'}$ 50–56 C_α–C_β 54–63	C_5–$C_{5'}$ 115–118	C_β–$C_{1'}$ 65–69 (for open structure)	C_4–O–C_5 78–83

a—biphenyl, b—dibenzodioxocin

reported that native lignins are relatively easier to depolymerise compared to technical lignins because of the presence of higher proportion of C–O inter-unit linkages [20].

1.3 Technical Lignins

Extracting native lignins from lignocellulosic biomass are future targets to achieve, currently available lignins, often called as technical lignins, are the by-products of conventional pulping routes such as kraft, soda, organosolv, hydrolysis and sulphite processes and they are called as kraft lignin, soda lignin, organosolv lignin, hydrolysis lignin and lignosulphonates respectively [35]. Organosolv is a general process where organic solvents such as ethanol, methanol, formic acid, acetic acid, ethylene glycol and tetrahydrofurfuryl alcohol are used to extract lignin [36]. As expected, all these lignins have different structures, often containing different impurities, depending on the pulping and pre-treatment or fractionation processes employed [37]. As mentioned before, native lignin contains a higher proportion of C–O inter-unit linkages, however during delignification (lignin fractionation) processes many C–C bonds are formed (Fig. 4). Generally, this is due to condensation reactions between compounds cleaved from the native lignin and remaining oligomers chains [38, 39]. In the case of the kraft pulping alkali-promoted condensation reactions take place forming alkali-stable linkages during the pre-treatment of the lignin [40]. Nevertheless, many researches are

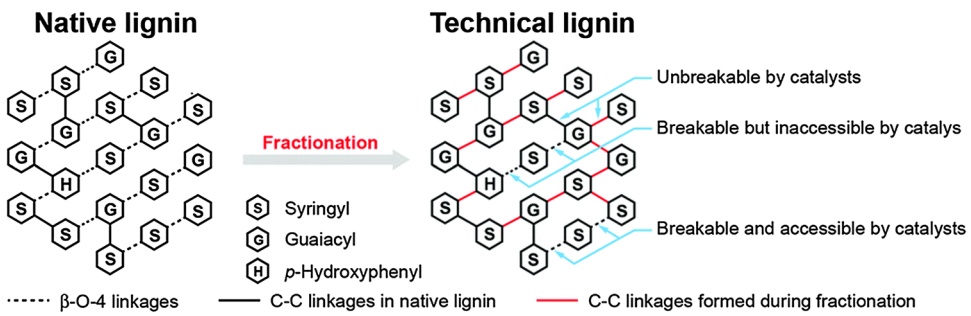


Fig. 4 Schematic representation for the formation of C–C bond during the delignification process. (Reproduced with permission from reference [39]. Copyright 2017, The Royal Society of Chemistry)

currently investigating the way to minimise this undesired condensation during delignification process by the stabilization of native lignin via addition of biological or chemicals capping agents, solvents, catalytic trapping pathways, and careful tuning of reaction parameters [18, 41]. For example, formaldehyde has been reported to be a good stabiliser, it react with alpha and gamma-hydroxyl groups on the lignin side-chain to form a stable 1,3-dioxane ring structure which prevents further condensation and hence the formation of new C–C linkages [42].

One of the major challenges in the catalytic processing these technical lignins is the presence of these impurities especially sulphur. For this reason, the extraction of technical lignin (delignification process) from biomass are classified into two types: (a) sulphur based processes and (b) non-sulphur based processes (Fig. 5) [37]. The disadvantages of sulphur containing lignin, resulting from sulphur based process, are the characteristic odour and are typically not suitable for catalysts containing noble metals, because sulphur poisons these catalysts. Therefore non-sulphur lignins (organosolv & soda lignin) are preferred for catalytic valorisation, however sulphur content can be beneficial for some specific catalytic processes where sulphided hydrodeoxygenation catalysts are used [43]. Because of the absence of sulphur, soda lignin and organolv lignins have been used as feedstock for catalytic valorisation reactions increasingly compared to kraft lignin [19]. Besides sulphur content, more physicochemical properties of technical lignins such as molecular weight, polydispersity, moisture, ash content, homogeneity, presence of certain functional groups have to be taken into consideration during feedstock selection for valorisation reactions [37, 44].

1.4 Lignin Valorisation

Depolymerisation of lignin to smaller molecular weight compounds is a very promising reaction, which can potentially generate value-added products, especially aromatics and functionalised aromatics. These aromatics can be used for the sustainable production of fuels, base chemicals and some high value fine chemicals [45]. Depolymerisation of lignin can be either catalytic or non-catalytic involving the breaking of C–O and C–C inter-unit linkages present in lignin. These depolymerisation reactions can be oxidative, reductive or redox-neutral. Typically, the oxidative depolymerisation reaction results in aromatic acids, aldehydes and occasionally aliphatic acids via the opening of aromatic ring [16]. The challenge in designing these strategies is to get the desired product(s) in high selectivity by selectively breaking specific inter-unit linkages in order to avoid complex separation processes.

To design strategies for the selective cleavage of inter-unit linkages, it is a common practice use lignin model compounds, to avoid the complexities such as the presence of impurities and heterogeneous structures involved in using whole lignin [37, 46]. These model compounds contain specific kind of inter-unit linkages that are present in lignin. A few examples of the model compounds, representing different inter-unit linkages in lignin that are typically used in literature are presented in Fig. 6 1-phenyl-2phenoxyethanol (1), pinoresinol (2), bibenzyl (3), benzofuran (4), diphenylether (5) and biphenyl (6) representing β–O–4, β–β, β–1, β–5, 4–O–5 and 5–5 linkages respectively. Lignin model compounds are very useful to study the kinetics and mechanism of these cleavage

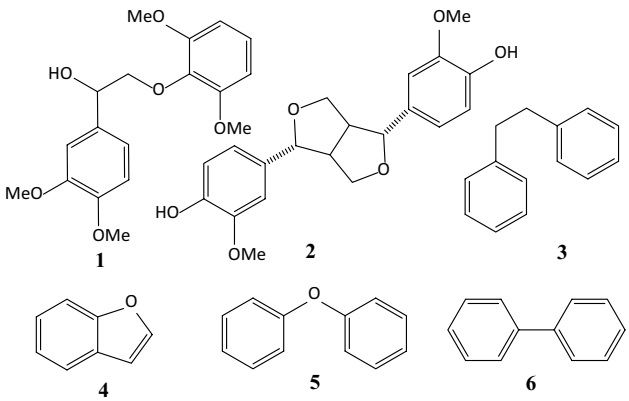


Fig. 6 Structures of some lignin model compounds that contain typical linkages present in lignin: 1 (β–O–4), 2 (β–β), 3 (β–1), 4 (β–5), 5 (4–O–5) and 6 (5–5)

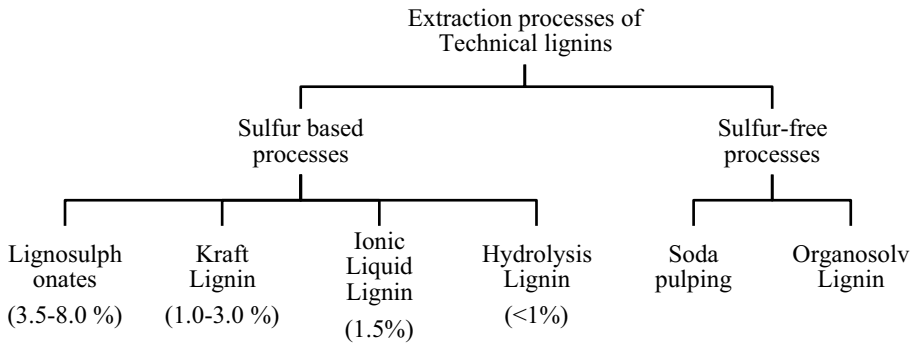


Fig. 5 Classification of delignification processes and the resultant technical lignin. The sulphur content in % is given within brackets for lignins from sulphur based processes. (Adapted from reference [37])

reactions. It is important to highlight that these lignin model compounds (Fig. 6) represent different inter-unit linkages in lignin and at the same time reducing the complexities involved in dealing with compounds with too many functionalities. These less complex model compounds are useful in designing catalysts for the breaking of inter-unit linkages and for in-depth studies on the mechanism of these catalytic reactions. However translating the catalytic results from these model compounds to real lignin is not straight forward as the presence of substituents and other functionalities severely complicate the process. However, these model compounds are a good starting point for catalyt development.

A number of articles have been published on the cleavage of C–O inter-unit linkages in model compounds; however reports on the cleavage of C–C inter-unit linkages are scarce because of their recalcitrant nature. However, breaking of C–C interunit linkages is crucial for the valorisation of technical lignins as they contain more C–C linkages than C–O linkages. For catalytic systems focussed on the cleavage of C–O linkages, readers are encouraged to read some excellent reviews on this subject [18, 47, 48]. Here we present a mini-review on the recently reported strategies for the catalytic cleavage of C–C inter-unit linkages in lignin model compounds as well as whole lignin (Fig. 7).

2 Catalytic C–C Bond Cleavage in Lignin Model Compounds and Technical Lignins

Catalytic conversion of the components of lignocellulosic biomass to chemicals and fuel components has been the subject of research efforts during the past decade resulting in a 20% annual increase in the number of publications on this subject [49]. Among these reports, catalytic depolymerisation of lignin has received greater attention recently. In the literature, six major strategies have been reported for the depolymerisation of lignin namely pyrolysis, hydrolysis, oxidation, hydrogenolysis, photocatalytic and enzyme catalysis (biocatalysis) [50]. Some of these routes like pyrolysis are thermal and non-catalytic while others are catalytic. Several catalytic routes including oxidative, reductive, redox neutral, photocatalytic and enzyme catalytic routes have been reported for the cleavage of C–O linkages, typically β–O–4 inter-unit linkage in lignin model compounds (Compound **1**, Fig. 6) [51]. However, in most cases, during these catalytic depolymerisation reactions C–C linkages are not broken [52]. In the literature, most of the reported C–C bond cleavages are the breaking of C_α–C_β and some examples of C_{Ph}–C_α bonds in the β–O–4 model compound **7** and in some other cases, breaking of the C_β–1 bond of the lignin model **8** (Fig. 8). However examples on the breaking of β–β [53], β–5 [54] and 5–5′ [55] linkages are scarce or not known in the literature. In general, these lignin model compounds, with different functional groups (OH or OCH_3 or OC_2H_5)

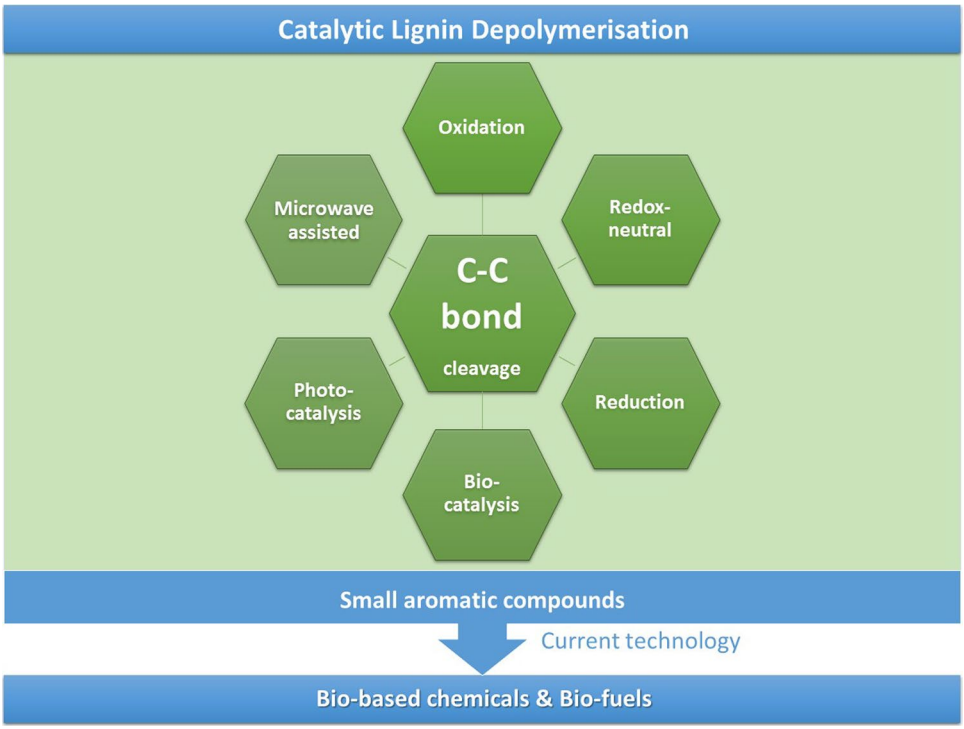


Fig. 7 Schematic representation of the motivation and the subtopics of this review

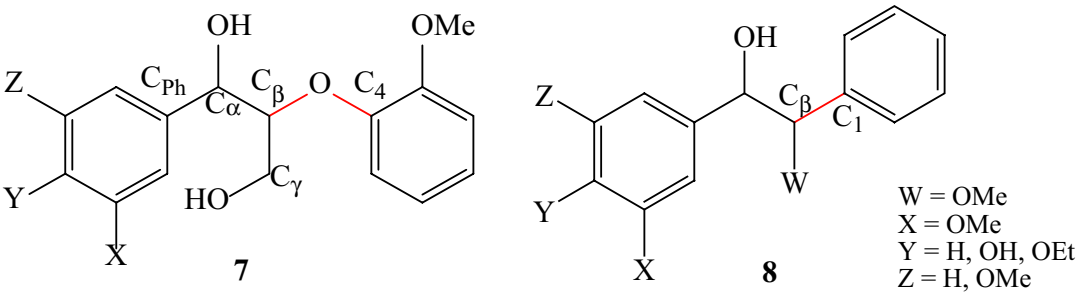


Fig. 8 Commonly used lignin model compounds containing β–O–4 linkage (methoxylated phenolic/non-phenolic dimer (β-aryl ether), **7**) and β–1 linkage (bibenzyl dimer, **8**). Other linkages including C–C linkages that can potentially break in these compounds are labelled

at different positions on the aromatic rings, are used as substrates (substrates 7 & 8 in Fig. 8), which are derivatives of model compounds **1** and **3** respectively (Fig. 6).

Through theoretical BDE calculation, Huang et al. proposed the cleavage of C_α–C_β linkage in lignin model compound **7** during its high temperature pyrolysis [29]. Here the authors describe the catalytic depolymerisation reaction where Co, Cu, Fe, Pd, V and Ru based metal complexes (some examples are given in Fig. 9) have been reported as active homogeneous catalysts for the cleavage of C–C bonds in some model compounds and in technical lignins. Besides homogeneous catalysts, supported metal catalysts, such as monometallic Pd, Pt, Rh, or Ru supported on carbon have also been reported as heterogeneous catalysts for the hydrogenolysis of lignin model compounds in supercritical water with some evidence for C–C bond cleavage. Other heterogeneous catalytic systems such as $CoMo/Al_2O_3$ catalyst, used in hydrodeoxygenation processes, and Pt/Al_2O_3, employed for aqueous-phase reforming of lignin, are also able to achieve the desired C–C bond cleavage. Specific examples of these homogeneous and heterogeneous catalysts are discussed in detail in the next sections.

For clarity, this catalytic C–C cleavage section has been sub-divided into (a) oxidative, (b) redox-neutral, (c) reductive, (d) microwave mediated and (e) enzyme and photo catalytic cleavage (Fig. 7).

2.1 Oxidative C–C Bond Cleavage

Catalytic oxidation is one of the most widely used methods for the breaking of the inter-unit linkages in lignin, especially C–C linkages because of the abundance of hydroxyl groups in lignin [54]. Behling et al. has reported an overview on the recent advances in the oxidative depolymerisation of

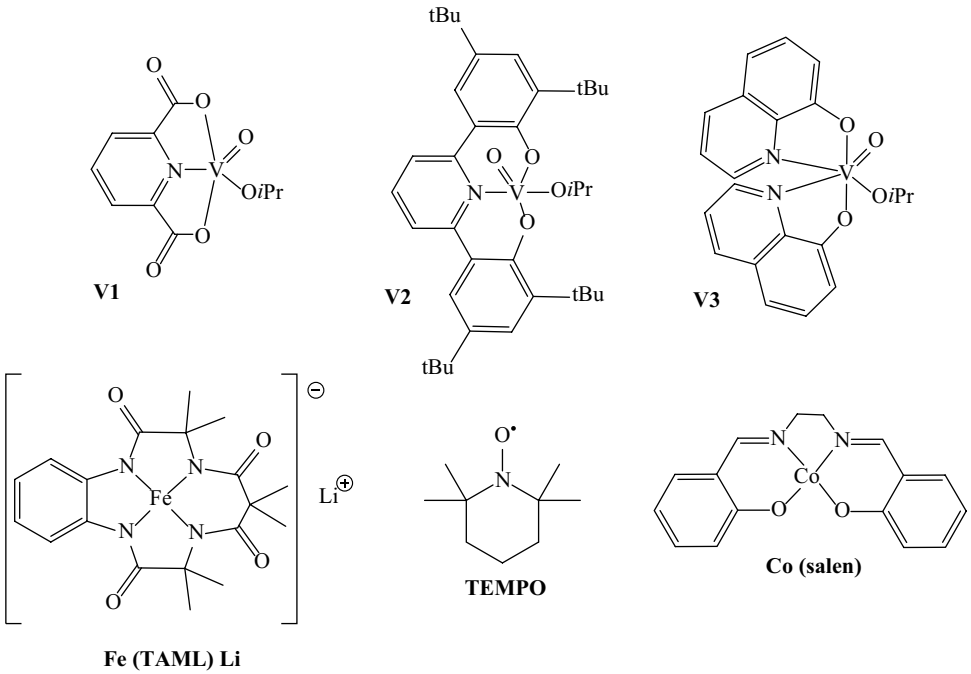
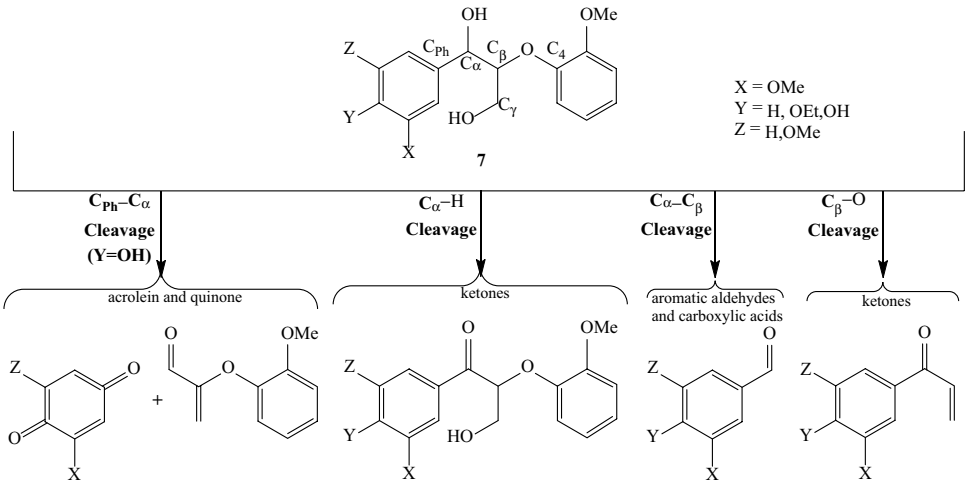


Fig. 9 Structures of some of the catalyst used for the oxidative C–C bond cleavage as described above

lignin including some oxidative C–C cleavages [55]. Paper and pulping industries use some of the most advanced oxidative routes for the depolymerisation and eventual removal of traces of lignin present in cellulosic materials [50, 55, 56]. Oxidative depolymerisation of lignins typically result in monomeric oxygenates like carbonyl compounds and carboxylic acids. Hanson et al. reported a general correlation between the oxidative breaking of specific linkage and the resultant product for the model compound **7** represented in Fig. 10 [57]. For example, C_α–C_β cleavage results in aromatic aldehydes (or corresponding carboxylic acid), while the C_α–H cleavage yields corresponding ketones, the breaking of C_β–O bond yields ketones and finally the C_{Ph}–C_α cleavage results in acrolein and quinone derivatives [58]. This correlation is useful to rationally design catalytic systems for the targeted cleavage of specific bonds to get specific compound in high yield.

Crestini et al. reported a catalytic, chlorine-free, oxidative cleavage of inter-unit linkages in an array of monomeric and dimeric, phenolic and non-phenolic lignin model compounds using a homogeneous methyltrioxorhenium(VII) ($MeReO_3$) (MTO) catalyst and H_2O_2 as the oxidant [59]. To study the C–C bond cleavage, they used different substituted lignin model compounds having β–O–4 units **9** and diphenylmethane units **10** as substrates (Fig. 11). The model compound **9**, used in this study, is a highly functionalised version of the simple model compound **1** (Fig. 6). During the catalytic reaction using phenolic model compound **9**, (substrate-1 in Fig. 11) > 98% of the substrate was converted to products. The products mixture includes carboxylic acid on the C_α position (4-hydroxy-3-methoxybenzoicacid), carbonyl group on the C_β position (hydroxyl-ketone), 2,6-dimethoxyphenol and muconolactone. Among these products, 4-hydroxy-3-methoxy benzoic acid was formed by the cleavage of C_α–C_β bond; however, the yield of this product was only 16%. Similarly, when substrates 2 and 3 (Fig. 11) were oxidised, evidence for the cleavage of the C_α–C_β bond was also observed [59]. The C_α–C_1 linkage present in **10** is not



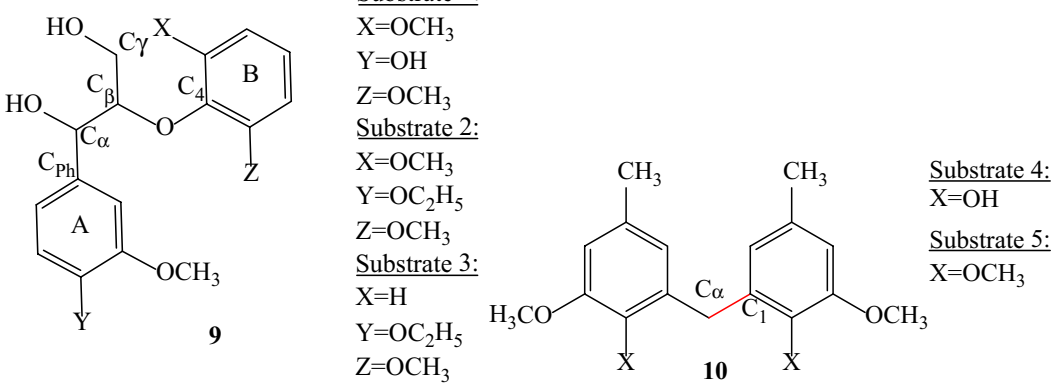


Fig. 10 Potential bond breakage pathways and possible products during the catalytic oxidation of lignin model compound **7**. (Adapted from reference [58])

Fig. 11 Phenolic and non-phenolic lignin model compounds with β–O–4 units (9) and diphenylmethane units (10) models for substrates 1–5. (Adapted from reference [59])

found in native lignins, however it is formed because of the condensation reactions during the delignification processes, hence it is prevalent in technical lignins [60]. In an effort to break this C_α–C_1 linkage, two versions of model compound **10** was oxidised using MTO and H_2O_2. For substrate 4 (phenolic model compound in Fig. 11) higher proportion of C_α–C_1 cleavage was observed resulting in aromatic carboxylic acids. For the substrate 5 (non-phenolic model compound in Fig. 11) only trace amount of C_α–C_1 cleavage was observed. They have concluded that C_α–C_1 cleavage is easier in phenolic model compounds, compared to non-phenolic compounds.

Encouraged by these results, Crestini et al. depolymerised technical lignins such as hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and hardwood organosolvent lignin (OSL) using MTO and H_2O_2 [59]. This catalytic oxidation reaction resulted in a decrease in the content of aliphatic OH groups (43, 14 and 67% reduction in SCL, OSL and RSL, respectively) and resulting in the formation of more soluble lignin fragments and higher yields monomeric carboxylic acids. Because of this additional C–C cleavage for this catalytic system, it is effective for the depolymerisation of complex technical lignins.

Hanson et al. reported the cleavage of C_{Ph}–C_α, C_α–C_β and β–1 inter-unit linkages during the aerobic oxidation of different lignin model compounds **7** and **8** (Fig. 8) using different vanadium metal complexes [61, 62]. During the aerobic oxidation of derivatives of model compound **8** with β–1 linkage using $(HQ)_2V^V(O)(O^iPr)$ (HQ = 8-oxyquinolinate) catalyst, they observed substantial C_{Ph}–C_α and β–1 cleavage [61]. Again, phenolic model compounds resulted in substantially higher C–C cleavage compared to non-phenolic model compounds and the solvents altered the product distribution. In DMSO solvent benzaldehyde and methanol were the major products, while in pyridine solvent the main products obtained were benzoic acid and methyl benzoate (Fig. 12) [61].

More recently, Ma et al. reported the selective oxidative C–C cleavage in model **1** using $VO(acac)_2$ catalyst with molecular oxygen as the oxidant. They further show the effect of solvents on the selectivity with acetic acid being the most desired solvent for C–C cleavage [63]. Amadio et al. reported the oxidative cleavage of model compound **7** (Fig. 6, phenolic X, Z = OCH_3, Y = OH) using V3 in Fig. 9, where they have found the effect of solvent on the selectivity of C_{Ph}–C_α cleavage. The yield of the products as a result of the breaking of C_{Ph}–C_α bond follows the order ethylacetate > 2-methyl THF > pyridine > THF. When non-phenolic version of the model compound **7** (X = H, Z = MeO, Y = EtO) was used, C–C cleavage was not observed at all [58].

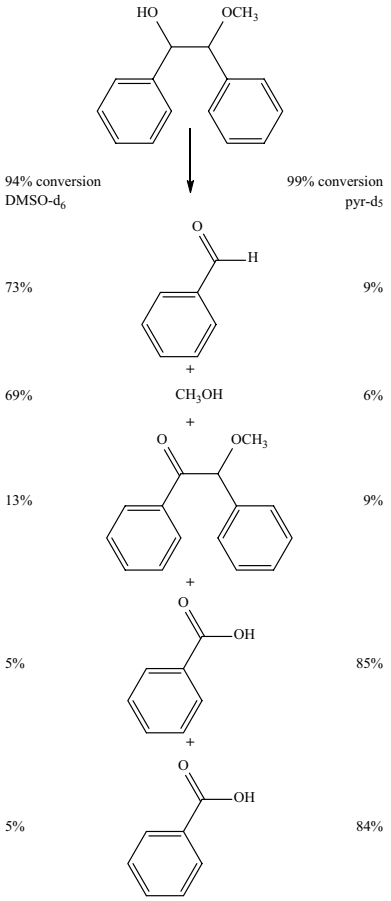


Fig. 12 Effect of solvent on products distribution during the oxidative cleavage of **8** using $(dipic)V^{IV}(O)(DMSO)_2$ catalyst in DMSO-d_6 (left hand side) and Pyridine-d_5 (right hand side). (Adapted from reference [61])

2.2 TEMPO Mediated Oxidative C–C Cleavage

TEMPO (2,2,6,6-tetramethyl-1-piperidin-1-yl-oxyl in Fig. 9) is used as it is or in combination with metal catalysts for the breaking of inter-unit linkages in lignin. Sedai and Baker reported an effective combined catalytic system containing CuCl and TEMPO for the oxidation of 1,2-diphenyl-2-methoxyethanol (model 8, W = OCH_3, Fig. 8), having β–1 linkage, using O_2 as the oxidant [64]. After 48 h reaction at 100 °C, they achieved more than 80% of β–1 cleavage. However, under similar condition, when $(dipicolinate)V^V(O)(O^iPr)$ **V1** (Fig. 9) was used as catalyst, the oxidation of secondary alcohol to ketone was followed by β–1 cleavage in a two step process. However when the intermediate ketone was oxidized by **V1**, > 90% of cleavage was observed. The CuCl + TEMPO catalytic system is more effective and better than the vanadium catalyst in breaking the β–1 bond in one step. The same group reported Cu(OTf)/2,6-lutidine/TEMPO catalyst system for the aerobic oxidation of model compound **8** having β–1 linkage [65]. In comparison to

vanadium complexes, generally this Cu catalyst is superior in breaking C–C linkages for non-phenolic models [65, 66]. For phenolic β–1 model compounds, catalytic amounts of TEMPO were not effective in breaking any C–C linkages, however when stoichiometric amounts of TEMPO were used substantial amount of C_{Ph}–C_α cleavage was observed [65]. When non-phenolic β–1 model compounds were tested, even with catalytic amounts of TEMPO substantial amount of C_α–C_β bond is broken. From these results we can conclude that for effective cleavage of C–C bonds, CuOTf + TEMPO (stoichiometric) system is more suitable for phenolic model compounds, whereas catalytic amount CuOTf + TEMPO is preferred for non-phenolic model compounds. When a 1:1 mixture of non-phenolic β–1 and β–O–4 model compounds (**7** and **8**) was used for the oxidation reaction using this catalytic system, substantial amount of C–C cleavage was observed and β–1 model compound got converted more readily compared to the β–O–4 model compound [65]. Rahimi et al. used catalytic amount of 4-acetamido TEMPO, without any metal, for the oxidation of β–O–4 model compound **9** using O_2 (Fig. 13). In this reaction, C_α–C_β cleavage has been clearly observed. This oxidation methodology has been extended to the depolymerisation of real lignin (Aspen lignin). Through detailed analysis of the product mixture, they propose C–C inter-unit cleavage [67].

Díaz-Urrutia et al. compared the catalytic activities of a few vanadium complexes for the oxidative depolymerisation of organosolv lignin and studied the mechanism of the catalytic oxidative cleavage using model compounds. Among all the tested catalysts, only bis(8-oxyquinoline) oxovanadium (V3) (Fig. 9) resulted in C–C cleavage under basic condition. However, under their reaction conditions, CuOTf + TEMPO and TEMPO did not result in C–C cleavage [68, 69]. Another interesting method for the cleavage of C_α–C_β linkage was reported by Patil et al. [70, 71]. Using simple model compounds, in the first step they have oxidised the OH group in C_α in β–O–4 model compound to form ketone using TEMPO/O_2 system. In the second step they converted the ketone to ester using Baeyer–Villiger oxidation (i.e. introducing O in between C_α and C_β), which is then hydrolysed in situ to form carboxylic acid, aldehyde and phenol (Fig. 14). Though this indirect method of breaking C_α–C_β is interesting, it will be less applicable for the depolymerisation of pure lignin [70].

Another two step strategy was proposed by Wang et al. for the cleavage of C_α–C_β bond in β–O–4 lignin model compound **1** (Fig. 6). In the first step, the secondary OH group is oxidised to ketone using $VOSO_4$/TEMPO catalyst and O_2 as oxidant. In the second step, the ketone is converted to monomeric phenols and carboxylic acids through the cleavage of C_α–C_β bond using Cu/1,10-phenanthroline catalyst and O_2 as oxidant [72]. The bond energy of the C_α–C_β bond decreases from 307.7 kJ mol^{-1} for the alcohol to 205.5 kJ mol^{-1} for the ketone, making the ketone an easier substrate for C–C cleavage [72]. More recently, the same group developed $Cu(OAc)_2/BF_3{\cdot}OEt_2$ catalyst for the cleavage of C_α–C_β bond in β–O–4 model compound **1** to produce esters and phenols [73]. Napoly et al. reported Fe (TAML) Li (Fe tetraamido macrocyclic complex) catalyst for the oxidative cleavage of C_α–C_β bond in β–O–4 model compound **1** using (diacetoxyiodo) benzene (DAIB) as the oxidant at 25 °C (Fig. 15) [74].

They futher report that by increasing the water content in the reaction mixture from 5% to a 20% the extent of C_α–C_β bond cleavage increased from 45 to 95%. Though the exact role of water in increasing the selectivity of C_α–C_β bond cleavage is not clearly understood. They have extended this methodology for the cleavage of β–1 linkage as well in a lignin model compound similar to **8** [74].

Luo et al. developed a transition-metal free protocol for the selective oxidative C–C cleavage in lignin model compounds with sodium persulfate as the oxidant [75]. They tested this system for the oxidative cleavage of different inter-unit linkages in many model compounds. Relevant to this review, using sodium persulfate, Luo et al. were able to

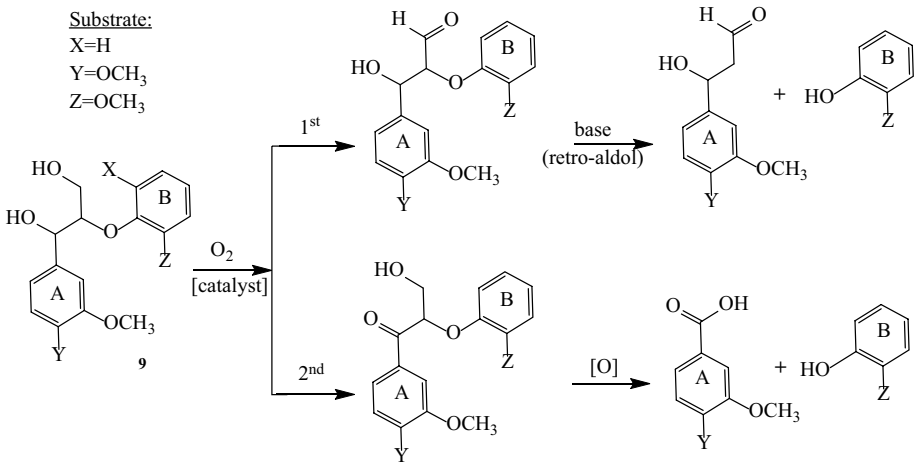


Fig. 13 Schematic representation of the chemoselective oxidation of β–O–4 model compound (**9**) using TEMPO and O_2. (Adapted from reference [67])

break β–1 linkage in model compound **3** into benzaldehydes in fairly good yields (ca. 60%). However, they could not translate this methodology for the oxidative depolymerisation of real lignins because of their poor solubility. Cobal salen [Co(salen)] complexes have also been used as homogeneous catalysts for the oxidative cleavage of phenolic and non-phenolic phenylcoumaranes (lignin model compound **4**), resulting in the cleavage of β–5′ inter-unit linkages to form benzoquinone derivatives, alkylphenyl ketones, benzoic acid derivatives and densely functionalized phenoxyacrylaldehydes. Some quantities of benzofuran (with β-5′intact) has also been found [76]. Biannic and Bozell used Co-Salen complexes for the selective cleavage of the C_{Ph}–C_{α} bond cleavage in β–O–4 model compound instead the typically weaker β-aryl ether linkage (C–O linkage) (Fig. 16). This oxidative cleavage reaction was performed at a milder reaction condition compared to other reported examples. This is one of the few examples where C–C bond is broken selectively compared to the C–O bond [77].

Mottweiler et al. reported the catalytic oxidative depolymerisation of organosolv beech and kraft lignins using transition-metal-containing hydrotalcites or combinations

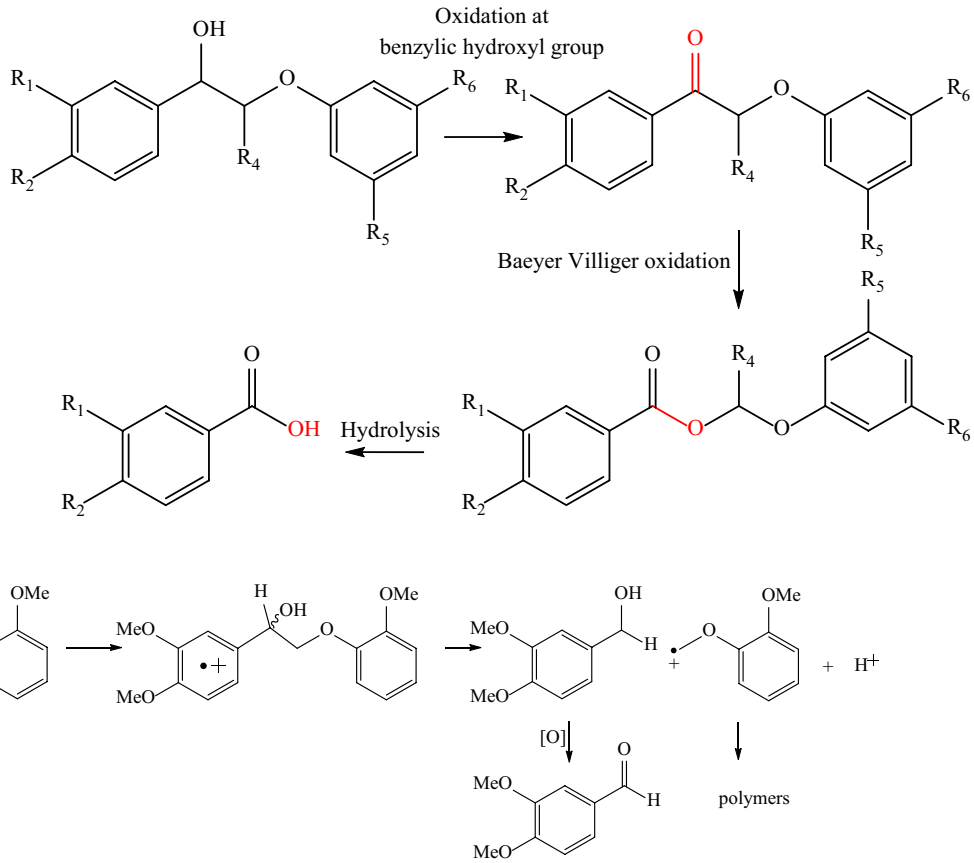


Fig. 14 Schematic representation of the two-step method for the breaking of Cα–Cβ bond via Baeyer–Villiger (BV) oxidation. (Adapted from reference [71])

Fig. 15 C_{α}–C_{β} bond cleavage in β–O–4 model compound **1** using Fe (TAML) Li as catalyst and DAIB as the oxidant at 25 °C Adapted from reference [74]

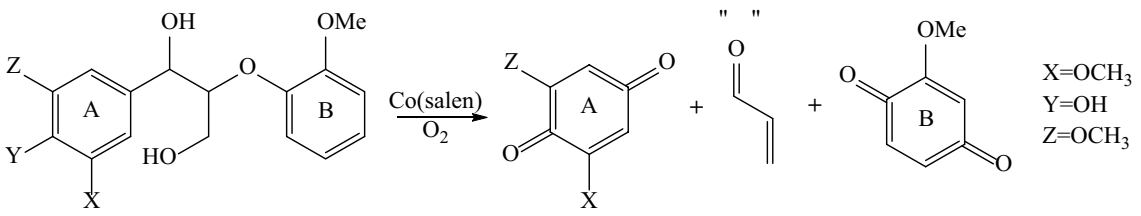


Fig. 16 Cobalt salen catalysed selective oxidative cleavage of C_{Ph}–C_{α} linkage in β–O–4 model compound to form benzoquinones. (Adapted from reference [77])

of vanadium and copper species using $V(acac)_3$ and $Cu(NO_3)_2{\cdot}3H_2O$ as catalysts using O_2 [78]. Significant reduction in the molecular weight was observed due to the effective cleavage of β–O–4 and other inter-unit linkages. The structure of the modified (depolymerised) lignin post reaction could not be fully understood by NMR, however, based on the resinol structure, they have confirmed that the cleavage of β–β inter-unit linkage. This is again one of the very few examples where β–β inter-unit linkage is broken.

2.3 Redox-Neutral C–C Bond Cleavage

In the case of Ru, specially Ruthenimun-triphos-based complexes such as $Ru(H)_2(CO)(PPh_3)$(xantphos) have been found to be effective in breaking the C–O bond in β–O–4 lignin model compound **7** [79]. However, it was not effective in breaking the C–C bond until vom Stein et al. reported a two-step redox neutral process for the cleavage of C–C linkages in lignin model compound **7** (Fig. 8). This redox neutral process involves a dehydrogenation-initiated retro-aldol reaction for the C_α–C_β bond clevage in different substituted lignin model compounds containing β–O–4 linkage (Fig. 17) [80].

2.4 Reductive C–C Bond Cleavage

Another catalytic route for the cleavage of C–C interunit linkage in lignin model compounds is the reductive pathway. Reports on the oxidative cleavage of lignin model compounds are dominated by homogeneous catalysts, whereas for the reductive cleavage of C–C bonds (hydrogenolysis) heterogeneous catalysts are more commonly used. Surprisingly, the first report on the hydrogenolysis of Aspen lignin over copper–chromium catalyst under relatively harsh conditions (220 atm of H_2 pressure at 260 °C) dates back to 1938 by Harris et al. [81]. Later on, the hydrogenolysis of technical lignins such as organosolv lignin was inspired by the hydrocracking processes developed in the petroleum refineries [82, 83]. During the lignin hydrocracking process mainly β–O–4 and C_{Ph}–C_α linkages are broken [82]. Oxidative routes are preferred to produce monomeric compounds used in the synthesis of bulk and fine chemicals since the resultant monomeric products are mostly oxygenates. However, hydrogenolysis is preferred to produce alkanes to be used for fuel applications. Huber and Corma also investigated the catalytic cracking of lignin using biomass-derived feedstocks mixed with petroleum-derived feedstocks and triglyceride-based feedstocks as substrate [84]. Catalytic hydrogenolysis of C–O linkages are known in the literature, however reports on the hydrogenolysis of C–C linkages in lignin model compounds are not common.

The catalytic hydrodeoxygenation (HDO) process is an interesting route to produce biofuels from biomass feedstock by removing oxygen. Jongerius et al. reported the HDO of lignin model compounds (derivatives of models **4, 6** and **7**) using $CoMo/Al_2O_3$ catalyst. During this HDO reaction, they report the breaking of C–C (β–5) linkage along with the breaking of C–O (β–O–4) linkage. However the 5–5′ linkage in the phenolic model **6** could not be broken under this condition (Fig. 18) [85].

The same group used 1% Pt/Al_2O_3 for the aqueous-phase reforming (APR) of technical lignin and found many monomeric compounds such as syringol or guiacol in the products mixture and proposed the cleavage of 5–5′ linkage (Fig. 19). Though this has not been confirmed by any studies using model compounds. To our knowledge, this is one of the first reports on the cleavage of 5–5′ linkage in the phenolic lignin model compound **6**, proved by the formation of methylguaiacol (7%) and guaiacol (12%) [86].

Yamaguchi et al. reported the cleavage of C–O and C–C bonds in β–O–4 model compound **7** and β–1 model compound **3** using many supported metal catalysts (Pd/C, Pt/C, Rh/C, or Ru/C) in supercritical water without any H_2. They report that the β–1 linkage is broken in supercritical water at 673 K using Rh/C catalyst, forming monomers such as toluene and benzene, which are valuable base chemicals [53].

2.5 Microwave Assisted C–C Bond Cleavage

Microwave irradiation is an alternative route that has been reported to be promising for lignin depolymerisation [6]. This process was studied on simple lignin models and on organosolv lignin using different supported metal (Ni, Pd, Pt and Ru) nanoparticles on mesoporous Al-SBA-15. A 10 wt%

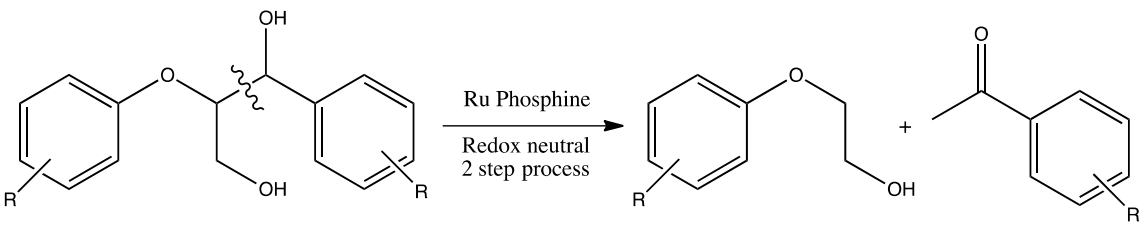


Fig. 17 Schematic representation of the selective cleavage of C_α–C_β bond in a β–O–4 model compound using a Ru phosphine complex. (Adapted from reference [80])

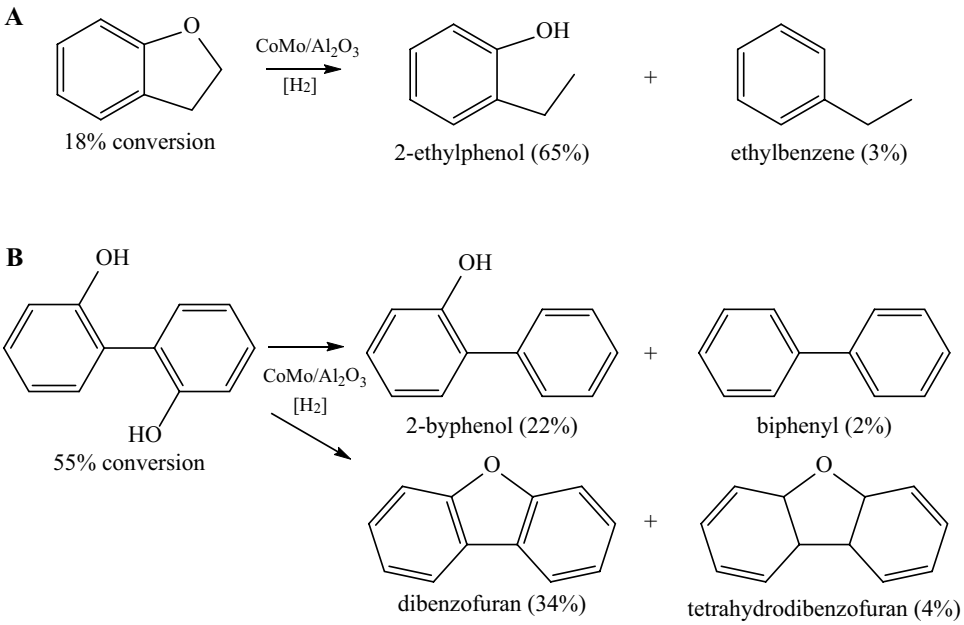


Fig. 18 Catalytic hydrodeoxygenation of **a** coumaran (β–5 inter-unit linkage) and **b** 2,2′-biphenol (5–5′ inter-unit linkage) using $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure for 4 h. (Adapted from reference [85])

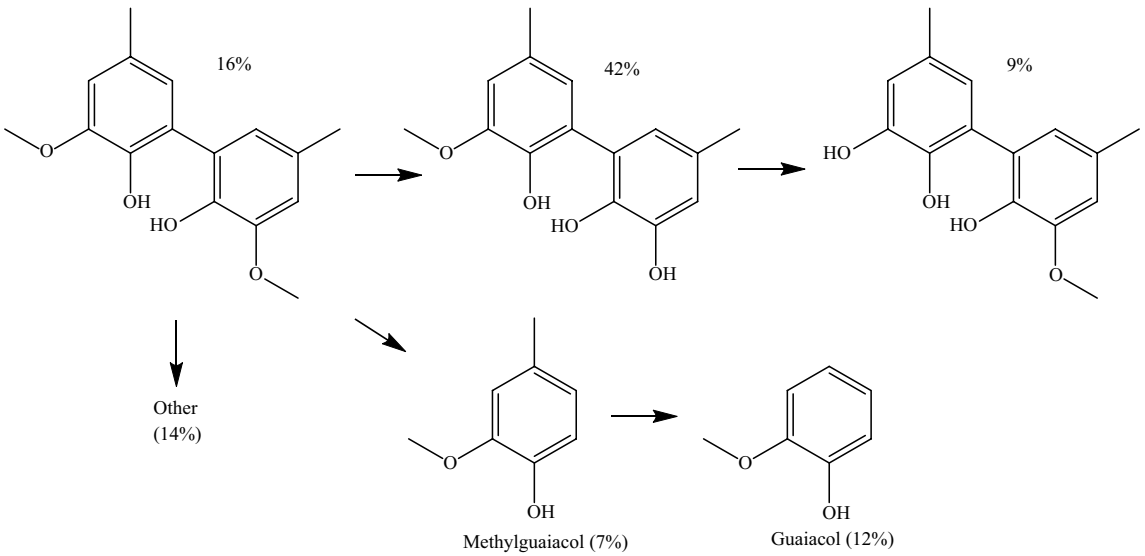


Fig. 19 Products obtained from the APR of **6** using 1% Pt/Al_2O_3. The formation of methylguaiacol and guaiacol confirm the cleavage of 5–5′ linkage. (Adapted from reference [86])

nickel supported on mesoporous Al-SBA-15 was found to be the most active catalyst yielding 30% of bio-oil from organosolv lignin after half an hour of reaction using formic acid as hydrogen donor [87, 88]. Zhu et al. utilised the microwave assisted cleavage of inter-unit linkages in lignin model compounds using ferric sulphate $Fe_2(SO_4)_3$ and HZSM-5 as catalysts to produce aldehydes, secondary alcohol or ketone compounds [89]. Then, they extended this methodology for the catalytic depolymeristion of organosolv lignin to produce aromatic monomers (vanillin, syringaldehyde, methyl vanillate, and methyl syringate). They further report that these products are formed by the selective cleavage of C_α–C_β bond (promoted by the Fe^{3+}) over the C–O bond (Fig. 20) [90]. Compared to conventional heating, microwave heating resulted in a 48.9% increase in the cleavage of C_α–C_β bonds for Sigma lignin and this increase is more substantial for organosolv lignin (62.3%) [90]. This microwave assisted cleavage of inter-unit linkages in technical lignin appears to be an interesting approach, however, more work has to be done to further understand why microwave heating is more effective in breaking C–C bonds in lignin.

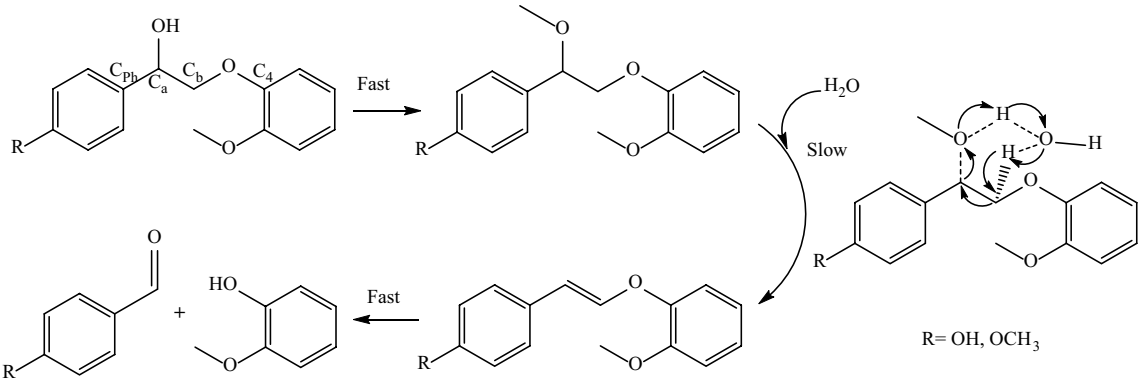


Fig. 20 Decomposition products during the microwave-assisted selective cleavage of the C_α–C_β bond in lignin model compound. (Adapted from reference [90])

2.6 Enzyme Catalysed and Photocatalytic C–C Bond Cleavage

Biocatalytic valorisation of low molecular weight lignin has been studied extensively and Abdelaziz et al. has reviewed this subject recently [91]. Tien and Kirk reported the first enzymatic degradation of spruce and birch lignins using *phanerochaete chrysosporium* and H_2O_2. In this they have reported the cleavage of C–C bonds in lignin model compounds [92]. This report inspired many research groups to work in the area of enzymatic degradation of lignin and lignin model compounds [93]. Through careful mechanistic investigation, Schoemaker et al. proposed a mechanism for this enzyme catalysed oxidative cleavage of C_α–C_β bond in β–1 lignin model compound involving single-electron transfer (SET) between aromatic rings resulting in a cationic radical of the substrate is formed [94, 95]. Inspired by these developments, Shimada et al. developed a tetraphenylporphyrinatoiron (III) chloride complex and tertbutyl hydrogenperoxide system for an unprecedented C–C bond cleavage in a non-phenolic β–1 lignin model dimer [94, 96]. They used 1,2-bis(4-ethoxy-3-methoxyphenyl) propane-1,3-diol, which is a combination of 2 β–O–4 linkages (model **1**) with a β–1 linkages (model **3**) as a model compound for this study. After these reports, enzyme catalysed oxidative depolymerisation has been widely studied, especially using peroxidases [97] and laccases [76]. An example of it is the use of peroxidase *pleurotous ostreaus* for the depolymerisation of lignosulfonate in the presence of a H_2O_2. Here they report the production of 2,6-dimethoxy-1,4-benzoquinone, benzoic acid, butyl phthalate, and bis(2-ethylhexyl) phthalate at ambient conditions [98]. These products are formed by the cleavage of many inter-unit linkages including C_α–C_β linkage [88, 98]. Cho et al. combined enzyme catalysis with photocatalysis for a highly regioselective C–C bond cleavage in β–1 and β–O–4 model compounds through cationic radicals generated through SET process [99, 100]. In this report, cation radicals were generated by using SET-sensitized photochemical and Ce(IV) and lignin peroxidase promoted oxidative processes. Photocatalytic methodologies have been used for the successful C–C bond cleavage recently. Mitchell and Moody reported the successful photocalytic cleavage of C–C linkages in a range of 1,2-diols and β–O–4 model compounds under visible light (solar) irradiation using 1,4-hydroquinone with a copper supported on aluminum oxyhydroxide catalyst (Cu/AlO(OH)) with oxygen as the oxidant [101]. In this system, the catalyst function as the electron transfer mediator (ETM) through the Cu(I)/Cu(II) redox couple.

3 Concluding Remarks and Future Prospects

One of the promising strategies, to produce aromatic compounds from sustainable feedstock, is to depolymerise lignin to smaller aromatic compounds. Lignin contains two inter-unit linkages namely C–O and C–C linkages and for the complete depolymerisation of ligin, it is important to break these two kinds of linkages effectively. Many catalytic and non-catalytic strategies have been reported for the breaking of C–O linkages, however reports on the effective breaking of C–C inter-unit linkages are scarce. This is because of the fact that the C–C inter-unit linkages are inherently stronger than the C–O linkages, hence tougher to break. However, all technical lignins (derived from paper and pulping industries) have higher proportion of C–C linkages than C–O linkages. Since technical lignins are available in huge quantities, it is important to design strategies to break the C–C linkages to achieve complete depolymerisation of technical lignins to smaller aromatic compounds. Here we review the reported strategies on breaking of C–C inter-unit linkages in lignin model compounds. Catalytic oxidation is the most widely used method for the cleavage of C–C bonds in lignin. However, other strategies such as hydrogenolysis, redox-neutral two step method, microwave assisted cleavage, biocatalytic

and photochemical routes have also been reported for the breaking of C–C bond. Inspite of a number of reports on the breaking of C–C bonds, strategies to break typical interunit C–C linkages like β–β and 5–5′ have not yet been reported. The aim of this review is to motivate researchers to design new catalytic methologies to break these inter-unit linkages using model compounds. Then, based on the abundance of C–O and C–C linkages an integrated approach towards the complete depolymerisation of lignin (native or native like and technical) to smaller aromatic compounds should be designed to realise the dream of a green and sustainable society.

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